Numerically exact calculation of rovibrational levels of Cl^--H_2O

water + atom

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Overview of the talk

- Cl^--H_2O spectroscopy background. Two goals of this study:
  - exact rovibrational levels are computed on a good PES.
  - a testing ground for VdW systems with flexible monomers : a polyatomic monomer and an atom
- We test three methods to compute its rovibrational levels

1) Break apart the monomer : a collection of (two) vectors
   - This leads to spherical harmonics basis for each vector, standard for a 4-atom molecule

2) Treat the monomer as a whole : a rotating object with internal vibrations
   - This leads to inter-monomer Wigner basis and intra-monomer vibrational basis
   - Standard rovibrational coordinates and basis can be used for the monomer.

3) Use monomer vibrational wavefunctions as basis: best method

The last two methods are new.

Ionic-hydrogen bond in X^--H_2O: red-shifted

FEATURE ARTICLE

Prying Apart a Water Molecule with Anionic H-Bonding: A Comparative Spectroscopic Study of the $X^- \cdot H_2O$ (X = OH, O, F, Cl, and Br) Binary Complexes in the 600−3800 cm^{-1} Region

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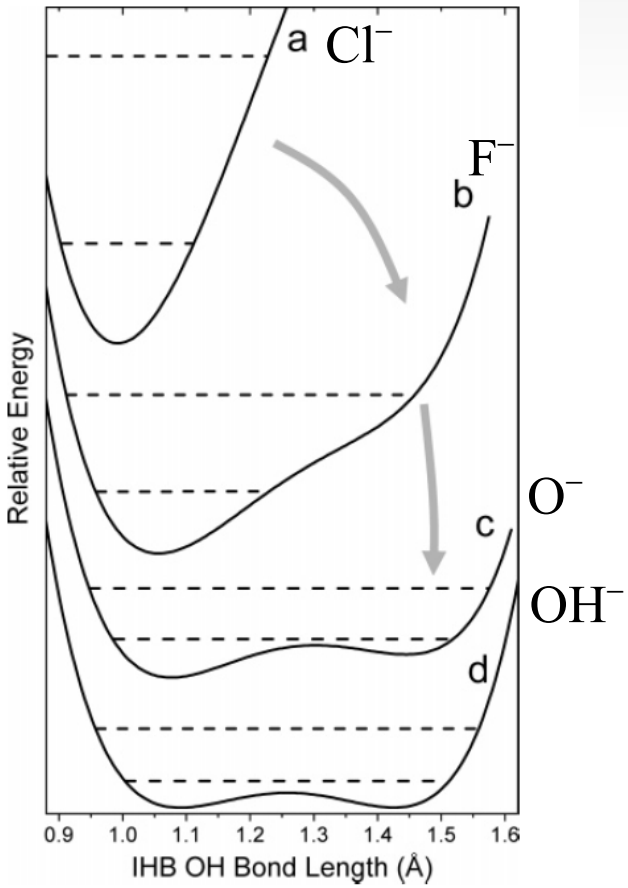
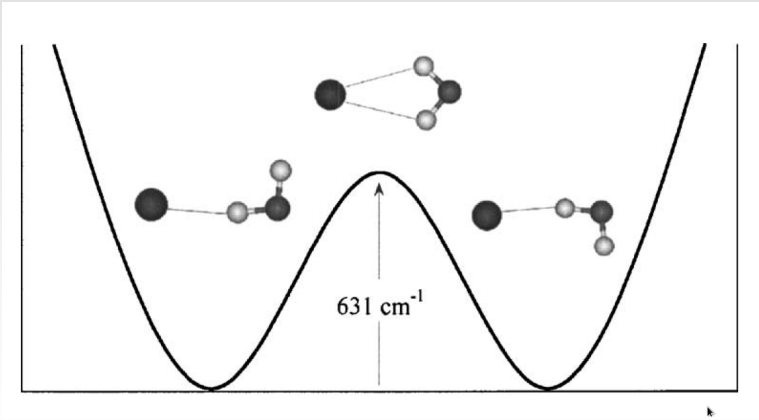


Overview

- M. A. Johnson group: Ar-messenger predissociation vibrational spectroscopy in the 600 – 3800 cm^{-1} region

Vibrational levels (in cm^{-1}) of Cl^-H_2O
[Horvath et al. J. Phys. Chem. A 114, 1556(2010)]

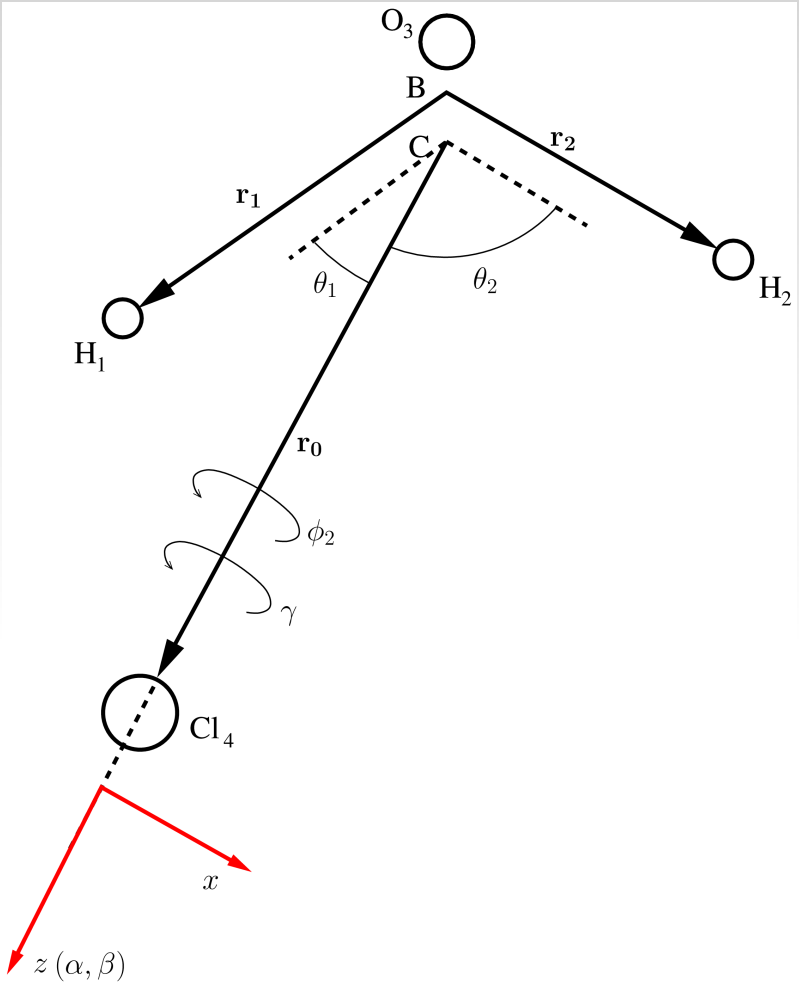
Band	Assignment	Expt.	Freq. shift
Cl^- dissociation	v_1	210.	
In-plane wag	v_2	309.	
Out-of-plane bend	v_3	738.	
HOH bend	v_4	1653.	+60.
Ionic OH stretch	v_5	3146.	-500.
Free OH stretch	v_6	3697.	-60.



in-plane wagging mode v_2
[Rheinecker and Bowman JCP, (2006)]

- Ionic hydrogen bond is red-shifted by 500 cm^{-1}
- A good surface: Rheinecker and Bowman JCP, 125, 133206(2006)
- Rheinecker and Bowman compute vibrational levels with **single-reference** Multimode but neglect the tunneling (barrier height is only 631 cm^{-1}). They also did **multi-reference** calculations but full results are not available.

Spherical harmonic basis: break apart the monomer



- Coordinates

  vibration : $r_0, r_1, r_2, \theta_1, \theta_2, \phi_2$; rotation : α, β, γ

- Basis (bend only)

  $|l_1(m_1)l_2m_2\rangle|JKM\rangle$

  where

$$\langle\theta_1,\theta_2,\phi_2|l_1(m_1)l_2m_2\rangle = \Theta_{l_1}^{m_1}(\theta_1)Y_{l_2}^{m_2}(\theta_2,\phi_2)$$

$$\langle\alpha,\beta,\gamma|JKM\rangle = \sqrt{\frac{2J+1}{8\pi^2}}D^J_{MK(\alpha,\beta,\gamma)^*}$$

$m_1 = K - m_2$, K is shared to remove $1/\sin^2\theta_1$ singularity

- A standard method for computing 4-atom molecule rovibrational levels (Wang and Carrington, 2002 JCP)

$B_0 = 0.15 \ \ \mathrm{cm}^{-1}$

$B_1 = B_2 = 18.6 \ \ \mathrm{cm}^{-1}$

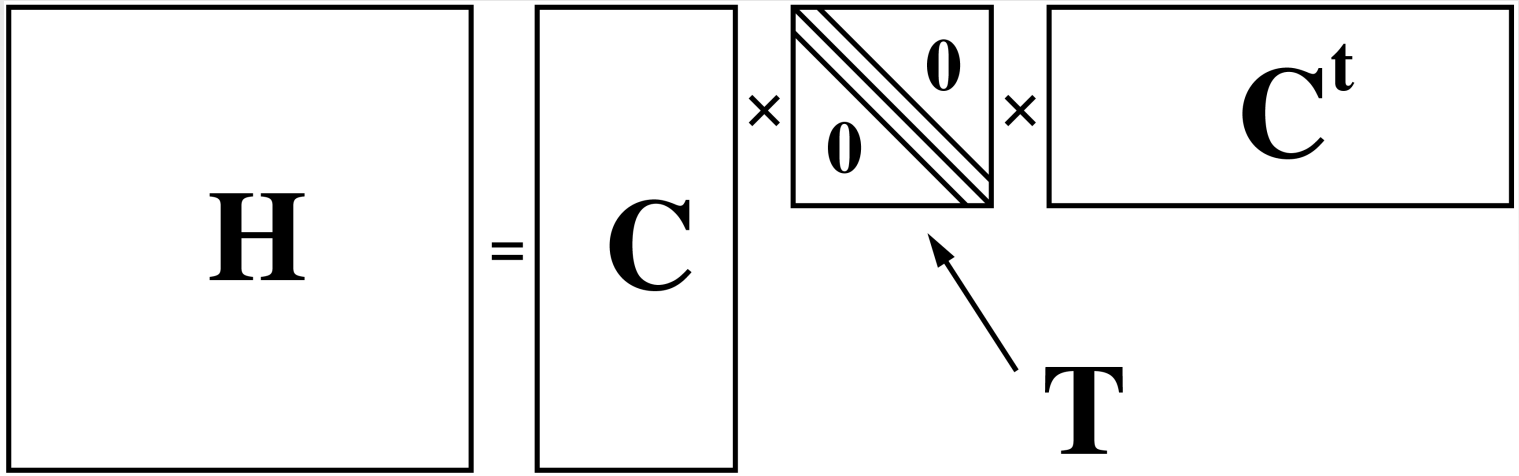
- A body-fixed (BF) frame attached to two vectors $\mathbf{r_0}$ and $\mathbf{r_1}$ whose orientation is (α, β, γ)
- Each vector of the monomer is represented with a pair of spherical polar angles (θ, ϕ) in the BF frame

Iterative eigensolver : Lanczos algorithm

- The Hamiltonian matrix is too large to diagonalize with millions of basis functions

$$f_{\gamma_0}(r_0) f_{\gamma_1}(r_1) f_{\gamma_2}(r_2) \Theta_{l_1}^{m_1}(\theta_1) \Theta_{l_2}^{m_2}(\theta_2) e^{m_2 \phi_2} / \sqrt{2\pi}$$

- Lanczos algorithm reduces a *large* Hamiltonian matrix **H** to a *small* tridiagonal matrix **T**



- One only needs to compute the matrix-vector product
- Employing the quadrature and structure of basis, the matrix-vector product is computed without storing any matrix elements of **H**.
- The potential matrix-vector product is computed via,

$$y_{\gamma_0,\gamma_1,\gamma_2,l_1',l_2',m_2'} = \sum_{\alpha_1} T_{\alpha_1,l_1'}^{m_1'} \sum_{\alpha_2} T_{\alpha_2,l_2'}^{m_2'} \sum_{\beta_2} T_{\beta_2,m_2'} V_{\gamma_0,\gamma_1,\gamma_2,\alpha_1,\alpha_2,\beta_2} \sum_{m_2} T_{\beta_2,m_2} \sum_{l_2} T_{\alpha_2,l_2}^{m_2} \sum_{l_1} T_{\alpha_1,l_1}^{m_1} x_{\gamma_0,\gamma_1,\gamma_2,l_1,l_2,m_2}$$

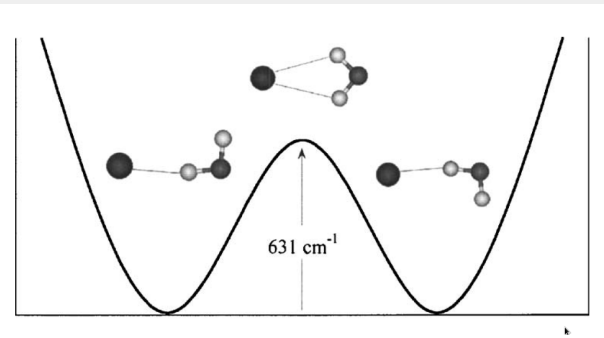
Quadrature matrix — Potential vector — Quadrature matrix

Results of spherical harmonics basis

Comparison of selected vibrational levels (in cm^{-1}) of Cl^-H_2O. ST and AT denote the symmetric and anti-symmetric tunneling states, respectively.

Band	Assignment	Expt.	Multimode	This work			
				ST		AT	
ZPE			5024.	5023.78	$A+$	0.35	$B+$
Cl^- dissociation	v_1	210.	205.	196.81	$A+$	197.26	$B+$
In-plane wag	v_2		362.	332.13	$A+$	345.98	$B+$
Out-of-plane bend	v_3	738.	715.	719.70	$B-$	720.64	$A-$
Out-of-plane bend	$2v_3$	1404.	1409.	1392.56	$A+$	1394.82	$B+$
HOH bend	v_4	1653.	1660.	1668.58	$A+$	1668.48	$B+$
HOH bend	$2v_4$	3289.	3308.	3310.71	$A+$	3311.76	$B+$
Ionic OH stretch	v_5	3146.	3123.	3117.52	$A+$	—	$B+$
Free OH stretch	v_6	3697.	3681.	3677.67	$A+$	3677.78	$B+$

Wang and Carrington, JCP, 140, 204306(2014)



- Computed with spherical harmonics basis, about 7.29 million functions for even parity

$$\max(l_1, l_2, m_2) = 25,\ \ N_{r_0} = 24, N_{r_1} = N_{r_2} = 7$$

- Single-reference Multimode results do not show tunneling splittings when the reference is at the bottom of one well [Rheinecker and Bowman, JCP, 125, 133206(2006)]
- The tunneling splitting between ST and AT is large : 14 cm^{-1} for v_2.

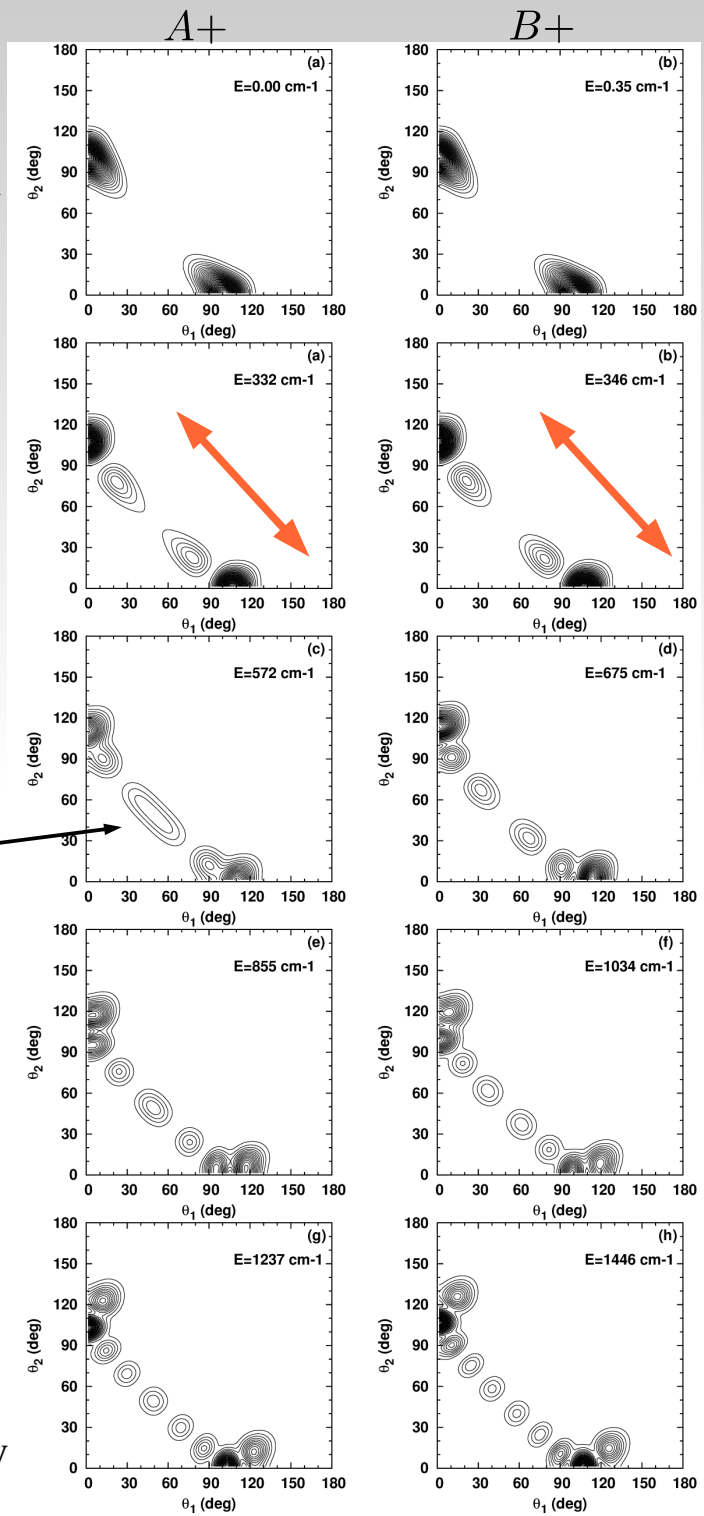
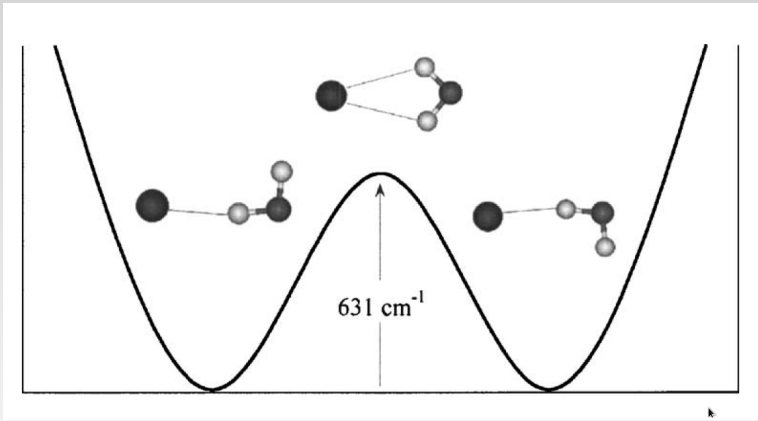


Figure 1: Overtones of the in-plane wag mode $v_2 = 0, \cdots, 4$.

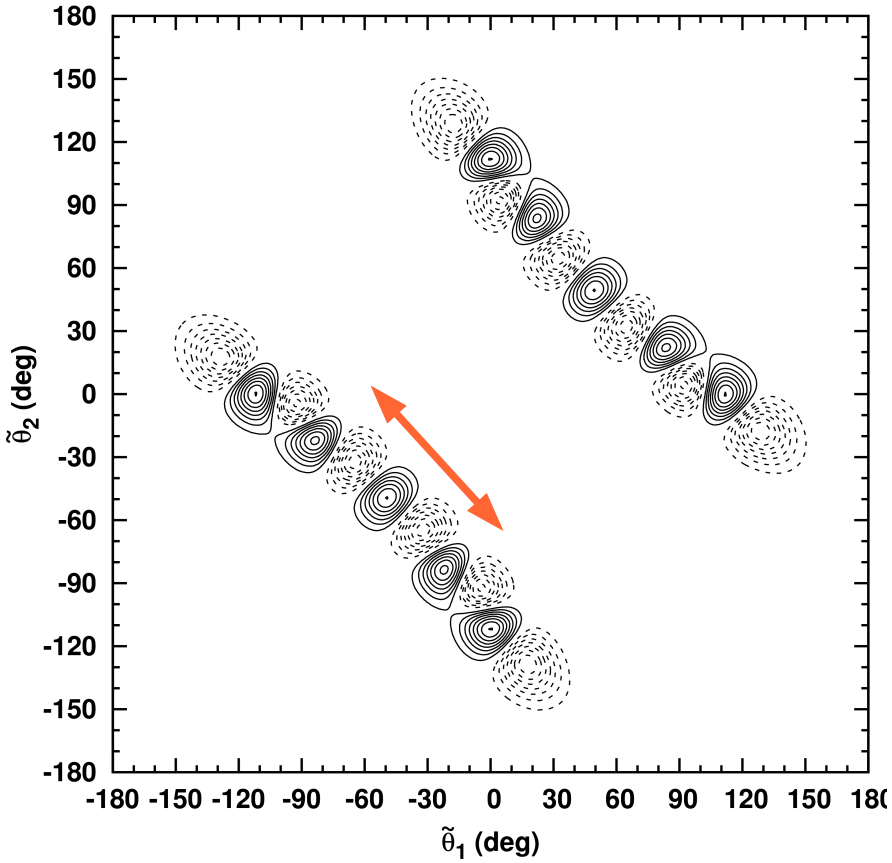


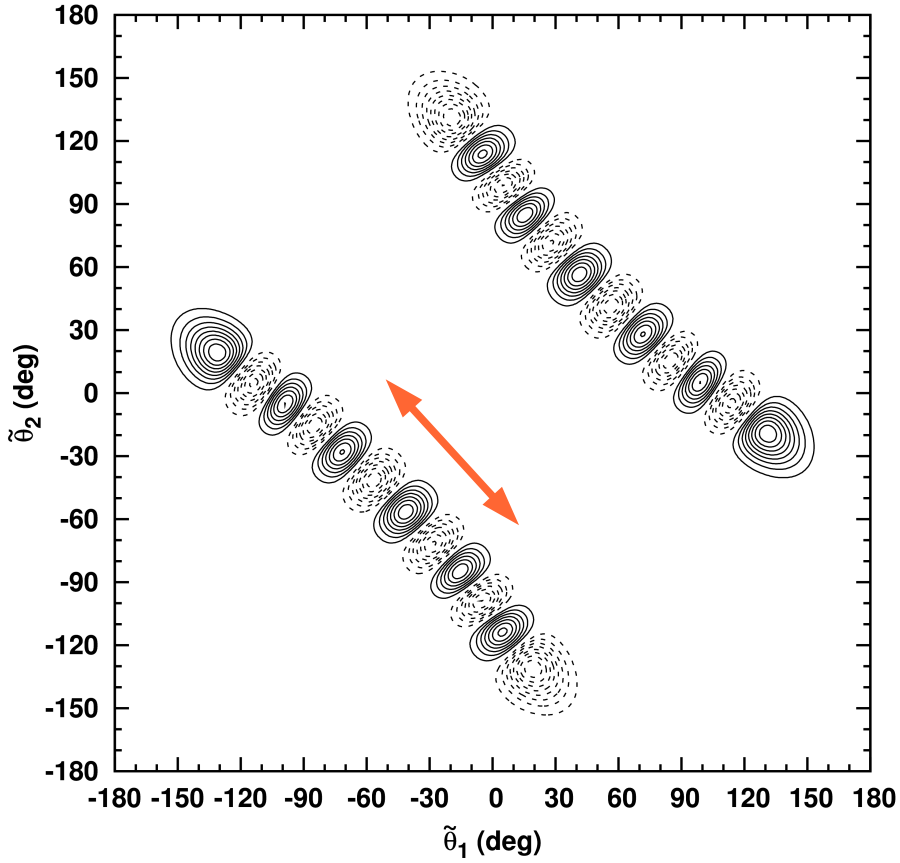
in-plane wagging mode v_2

- A typical double well behaviour.
- 631 cm^{-1} barrier height
- At v = 2 the wavefunctions already populate the top of the barrier
- The vibrational coordinate is

$$Q = \delta\theta_1 - \delta\theta_2$$

$A+$ $B+$





- The two tunneling wavefunctions of $v_2 = 5$ state at 1663 and 1891 cm^{-1}, plotted in extended angles : each shape appears twice
- The vibrational coordinate is $Q = \delta\theta_1 - \delta\theta_2$

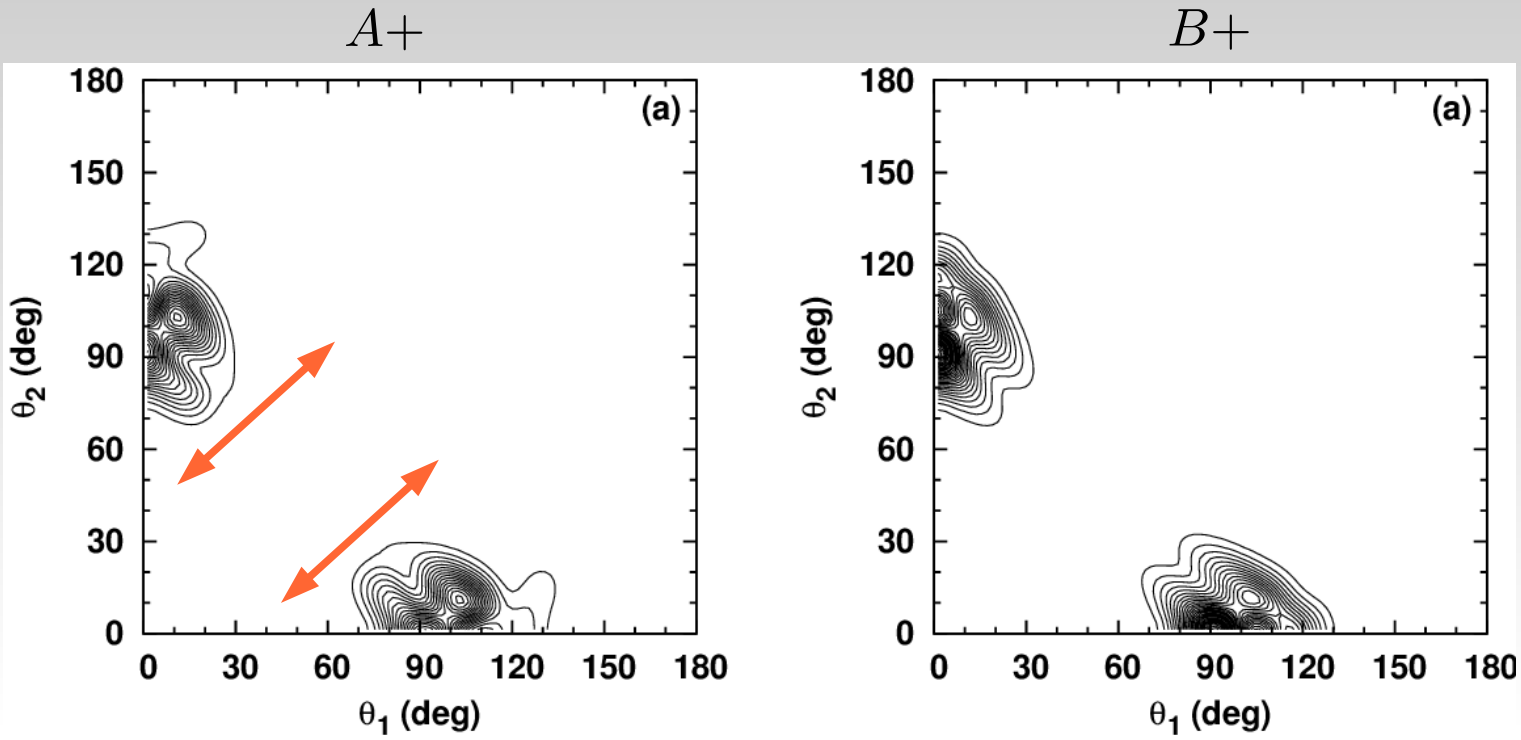
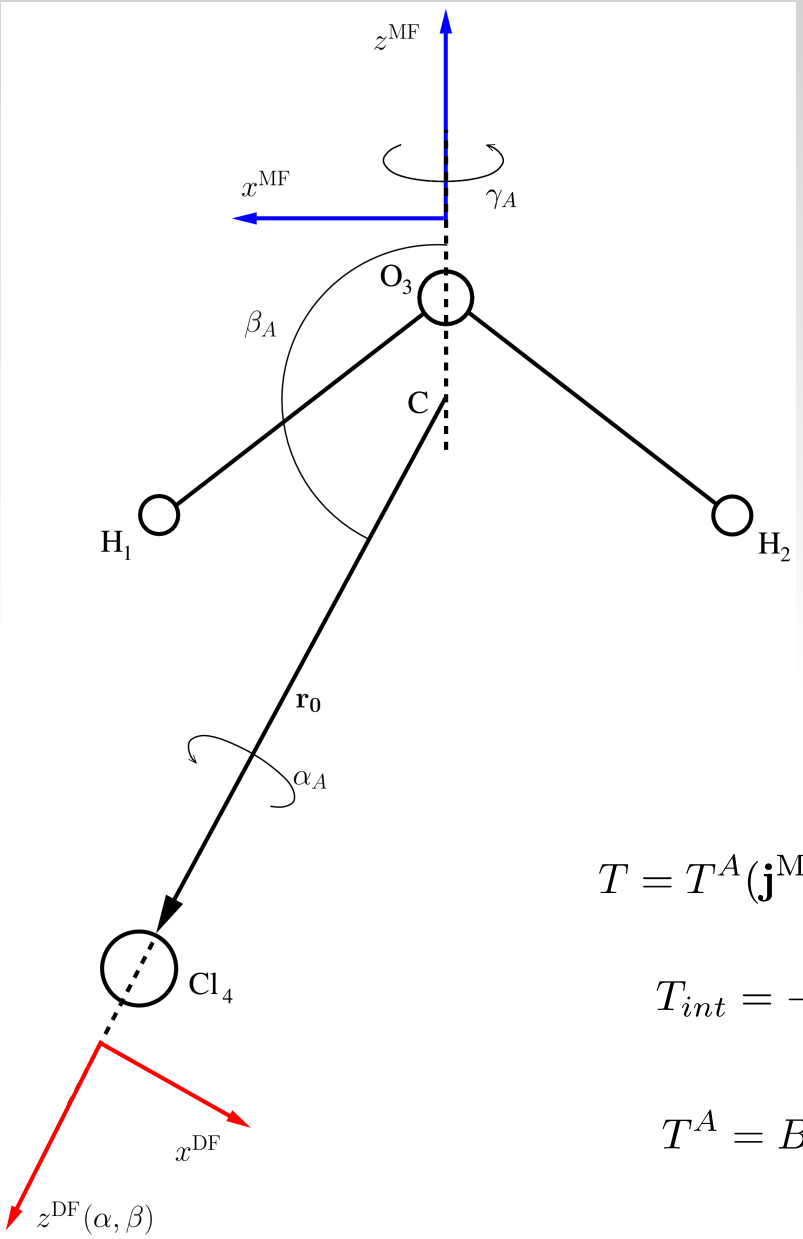


Figure 1: HOH bend $v_4 = 1$

- The two tunneling prob. densities of $v_4 = 1$ states at 1669 and 1668 cm^{-1}.
- The vibrational coordinate is $Q = \delta\theta_1 + \delta\theta_2$

Wigner basis for inter-monomer vibration (rigid monomer)



- Coordinates (Ar-H_2O, C. Leforestier, 1996 JCP)

  vibration : r_0, β_A, γ_A; rotation : α, β, α_A

- Basis (bend only)

  $|j_A k_A(m_A = K)\rangle |JKM\rangle$

$$\langle \alpha_A, \beta_A, \gamma_A | j_A k_A(m_A)\rangle = \sqrt{\frac{2j_A+1}{8\pi^2}} D^{j_A}_{m_A k_A}(\alpha_A, \beta_A, \gamma_A)^*$$

$$\langle \alpha, \beta, 0 | JKM\rangle = \sqrt{\frac{2J+1}{4\pi}} D^{J}_{MK(\alpha,\beta,0)^*}$$

$m_A = K$, K is shared to remove $1/\sin^2\beta$ singularity

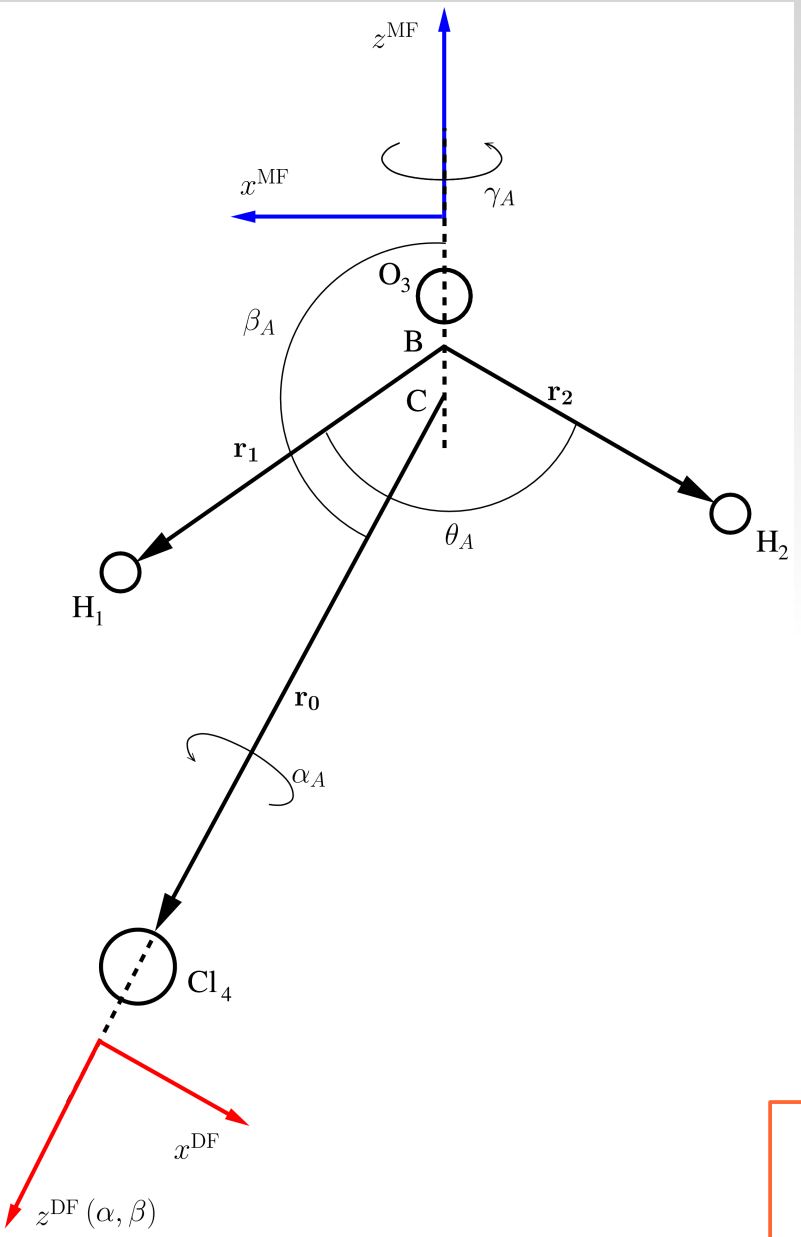
$$T = T^A(\mathbf{j}^{\mathrm{MF}}) + T_{int}$$

$$T_{int} = -\frac{1}{2\mu_0 r_0^2}\frac{\partial}{\partial r_0} r_0^2 \frac{\partial}{\partial r_0} + B_{r_0}(r_0)\left[J^2 - i\cot\beta\frac{\partial}{\partial\beta} + j^2 - 2\mathbf{j}\cdot\mathbf{J}\right]$$

$$T^A = B_x (j_x^{\mathrm{MF}})^2 + B_y (j_y^{\mathrm{MF}})^2 + B_z (j_z^{\mathrm{MF}})^2$$

- A dimer-fixed (DF) frame (red) for system rotation (α, β).
- A monomer-fixed (MF) frame (blue) for inter-monomer vibration (α_A, β_A, γ_A)

New method (I) : inter-monomer Wigner basis and intra-monomer vibrational basis



bisector-z embedding

- Coordinates $\theta_1, \theta_2, \phi_2 \longrightarrow \beta_A, \gamma_A, \theta_A$

  vibration : $r_0, r_1, r_2, \beta_A, \gamma_A, \theta_A$; rotation : α, β, α_A

- Shared-K FBR Basis (bend only)

$$\Theta_{l_A}^{k_A}(\theta_A)|j_A k_A(m_A = K)\rangle|JKM\rangle$$

K is shared to remove $1/\sin^2\beta$ singularity

k_A is shared to remove monomer singularity $1/\sin^2\theta_A$

- T^A is standard rovibrational triatomic KEO

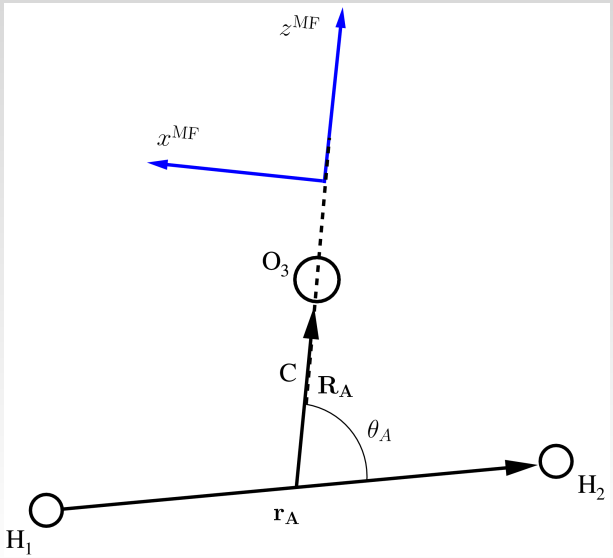
$$T = T^A(r_1, r_2, \theta_A; \mathbf{j}^{\mathrm{MF}}) + \mathbf{T_{int}}$$

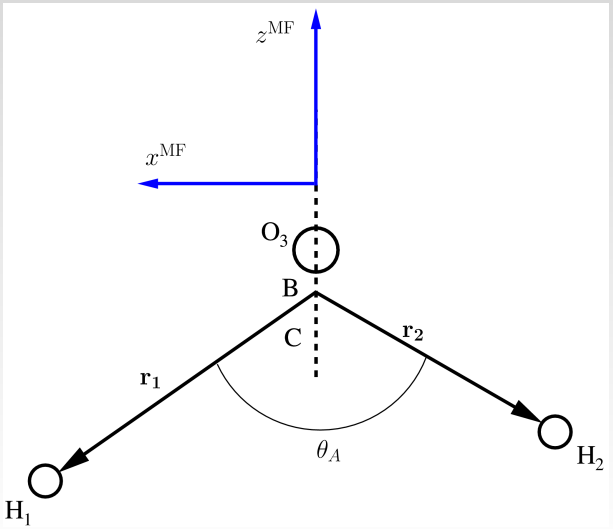
- Triatomic Coriolis coupling becomes vibrational momentum coupling

$$-\left[B_{r_1}(r_1) - B_{r_2}(r_2)\right] p_{\theta_A}^H j_y^{\mathrm{MF}}$$

- A dimer-fixed frame (red) for system rotation
- A monomer-fixed frame (blue) for internal rotation
- H-O-H bond angle is a new vibrational coordinate

Standard coordinates and embedding for triatomic molecules





- Jacobi coordinates and vector-z embedding
- Shared-K basis

$$\Theta_{l_A}^{k_A}(\theta_A)|j_A k_A m_A\rangle$$

- All KEO singularities are removed
- But momentum coupling is large.

- Radau coordinates and bisector-z embedding
- Shared-K basis (remove $\theta = \pi$ singularity)

$$\Theta_{l_A}^{k_A}(\theta_A)|j_A k_A m_A\rangle$$

- DVR basis ($\theta = 0$ and π singularity)

$$f_{\gamma_A}(\theta_A)|j_A k_A m_A\rangle$$

- Singularity only occurs at $\theta = \pi$ (not important).
- Momentum coupling is zero at equilibrium
- Chosen !

Method III (new): inter-monomer Wigner basis and vibrational wavefunction basis

- Use of vibrational wavefunction basis to solve rovibrational problem is an old idea and is popular in recent years : Carter and Bowman, Csaszar, Rey and Tyuterev etc.

$$|v\rangle|JKM\rangle$$

- Contracted from Radau-coordinates and bisector-z embedding and DVR basis,

$$f_{\gamma_1}(r_1)f_{\gamma_2}(r_2)f_{\gamma_A}(\theta_A)|j_A k_A(K)\rangle|JKM\rangle$$

- Use of monomer vibrational wavefunction as basis.

$$|v_A\rangle|j_A k_A(K)\rangle|JKM\rangle$$

- The momentum-momentum coupling is small

$$\langle v'_A \left| -[B(r_1) - B(r_2)]p^H_{\theta_A} \right| v_A\rangle j_y^{\mathrm{MF}}$$

Only one vibrational wavefunction is good for many systems and is already better than rigid-monomer approximation.

$$|v_A = 0\rangle|j_A k_A(K)\rangle|JKM\rangle$$

Results of Wigner basis

$A+$ vibrational levels of Cl^-H_2O calculated with different methods : primitive basis

state	SH basis[a]	Errors of Wigner basis	
		shared-K FBR	DVR
GS	5023.765	0.000	0.000
v_1	196.807	0.000	0.000
v_2	332.103	0.000	0.000
$2v_1$	387.813	0.000	0.000
v_1+v_2	519.606	0.000	0.000
$2v_2$	571.955	0.000	0.000
$3v_1$	573.258	0.000	0.000
$2v_1+v_2$	700.583	0.000	0.000
$4v_1$	751.907	0.000	0.000
v_1+2v_2	754.384	0.000	0.000
$3v_2$	854.914	0.000	0.000
$3v_1+v_2$	875.143	0.000	0.000
$5v_1$	925.563	0.000	0.000
$2v_1+2v_2$	931.216	0.000	0.000
N_{bas}(M)[b]	7.29	7.29	11.14
$E_{\max}$(K)	85	2600	4320
Basis	$\|l_1,(m_1),l_2,m_2\rangle$	$\|l_A;j_A,k_A,(m_A=0)\rangle$	$\|\gamma_3;j_A,k_A,(m_A=0)\rangle$

[a] SH (spherical harmonic) basis : Wang and Carrington, JCP, 140, 204306(2014)
[b] 1M = 10^6 and 1K = 10^3.

- The SH and Wigner basis sizes are equal.

  SH basis : $\max(l_1,l_2,m_2)=25$

  Wigner basis : $\max(l_A,j_A,k_A)=25$

- Wigner basis (shared-K FBR) and SH basis are based on different angles
- The efficiency of the Wigner basis is **similar** to that of the spherical harmonic basis because in both cases the coupling is proportional to B_0.
- 1323 (7 x 7 x 27) DVR points for monomer
- Singulariy is completely removed for SH basis. Thus smallest spectral range.

Results of monomer vibrational wavefunction basis

$A+$ vibrational levels of Cl^-H_2O calculated with different methods : monomer vibrational wavefunction basis

	SH[a]	Errors of $\|v\rangle$ basis (this work)				
state		N_v=10[b]	N_v=30	N_v=50	N_v=70	N_v=100
GS	5023.765	8.444	0.186	0.013	0.003	0.000
v_1	196.807	-0.522	-0.007	0.000	0.000	0.000
v_2	332.103	-0.737	0.079	0.009	0.002	0.000
$2v_1$	387.813	-0.967	-0.010	0.000	0.000	0.000
v_1+v_2	519.606	-1.275	0.069	0.009	0.003	0.000
$2v_2$	571.955	-1.783	0.058	0.009	0.002	0.000
$3v_1$	573.258	-1.477	-0.004	0.002	0.001	0.000
$2v_1+v_2$	700.583	-1.735	0.060	0.009	0.003	0.000
$4v_1$	751.907	-1.666	0.016	0.005	0.002	0.000
v_1+2v_2	754.384	-2.296	0.027	0.006	0.002	0.000
$3v_2$	854.914	3.072	0.313	0.035	0.010	0.001
$3v_1+v_2$	875.143	-2.125	0.052	0.010	0.003	0.000
$5v_1$	925.563	-1.872	0.009	0.005	0.002	0.000
$2v_1+2v_2$	931.216	-2.685	0.028	0.007	0.002	0.000
N_{bas}(M)	7.29	0.08424	0.253	0.421	0.590	0.842
E_{max}(K)	85	55	67	92	210	837

[a] SH (spherical harmonic) basis : Wang and Carrington, JCP, 140, 204306(2014)

[b] N_v the number of H_2O vibrational wavefunctions used as basis.

- N_v = 70 converge all levels within 0.01 cm^{-1}.
- Very efficient basis: basis with N_v = 70,
  - 11.14/0.59=19 times smaller than DVR basis
  - 7.29/0.59=12 times smaller than SH basis
  - small spectral range
- When coupling is weak for VdW system, a few vibrational functions are enough. Sometimes even one vibrational function (ground vibrational state) is good enough.

Results of monomer vibrational wavefunction basis : J>0

All $J = 1$ levels (in cm^{-1}) of Cl^-H_2O up to 500 cm^{-1} [a].

Energy	Assignment	Energy	Assignment
	$J = 1, A+$		$J = 1, B+$
19.1423	(gs, $B+$)	18.7845	(gs, $A+$)
215.9962	(ν_1, $B+$)	215.5431	(ν_1, $A+$)
363.9843	(ν_2, $B+$)	350.0015	(ν_2, $A+$)
407.1358	($2\nu_1$, $B+$)	406.4942	($2\nu_1$, $A+$)
	$J = 1, A-$		$J = 1, B-$
0.3059	(gs, $A+$)	0.6606	(gs, $B+$)
19.1408	(gs, $B+$)	18.7832	(gs, $A+$)
197.1083	(ν_1, $A+$)	197.5572	(ν_1, $B+$)
215.9946	(ν_1, $B+$)	215.5418	(ν_1, $A+$)
332.4093	(ν_2, $A+$)	346.2791	(ν_2, $B+$)
363.9809	(ν_2, $B+$)	350.0105	(ν_2, $A+$)
388.1091	($2\nu_1$, $A+$)	388.7461	($2\nu_1$, $B+$)
407.1342	($2\nu_1$, $B+$)	406.4929	($2\nu_1$, $A+$)

[a] SH (spherical harmonic) basis : Wang and Carrington, JCP, 2014

- benchmark levels obtained with SH basis
- Wigner basis: both shared-K FBR and DVR monomer basis give identical levels.

Errors of $J = 1$ levels (in cm^{-1}) with $N_v = 70$ basis functions.

Energy	Assignment	Energy	Assignment
0.0033	(zpe, $A+$)		
	$J = 1, A+$		$J = 1, B+$
-0.0001	(gs, $B+$)	0.0000	(gs, $A+$)
0.0000	(ν_1, $B+$)	0.0000	(ν_1, $A+$)
0.0032	(ν_2, $B+$)	0.0022	(ν_2, $A+$)
0.0003	($2\nu_1$, $B+$)	0.0002	($2\nu_1$, $A+$)
	$J = 1, A-$		$J = 1, B-$
0.0000	(gs, $A+$)	0.0000	(gs, $B+$)
-0.0001	(gs, $B+$)	-0.0001	(gs, $A+$)
0.0001	(ν_1, $A+$)	0.0001	(ν_1, $B+$)
0.0001	(ν_1, $B+$)	0.0000	(ν_1, $A+$)
0.0024	(ν_2, $A+$)	0.0033	(ν_2, $B+$)
0.0032	(ν_2, $B+$)	0.0023	(ν_2, $A+$)
0.0003	($2\nu_1$, $A+$)	0.0004	($2\nu_1$, $B+$)
0.0003	($2\nu_1$, $B+$)	0.0002	($2\nu_1$, $A+$)

- N_v = 70 converge all levels to about 0.001 cm^{-1}.

Results of monomer vibrational wavefunction basis : J>0

Errors of $J = 1$ levels (in cm^{-1}) with $N_v = 100$ basis functions.

Energy	Assignment	Energy	Assignment
0.0004	(zpe, $A+$)		
	$J = 1, A+$		$J = 1, B+$
0.0000	(gs, $B+$)	0.0000	(gs, $A+$)
0.0000	(ν_1, $B+$)	0.0000	(ν_1, $A+$)
0.0003	(ν_2, $B+$)	0.0001	(ν_2, $A+$)
0.0000	($2\nu_1$, $B+$)	0.0000	($2\nu_1$, $A+$)
	$J = 1, A-$		$J = 1, B-$
0.0000	(gs, $A+$)	0.0000	(gs, $B+$)
0.0000	(gs, $B+$)	-0.0001	(gs, $A+$)
0.0000	(ν_1, $A+$)	0.0000	(ν_1, $B+$)
0.0000	(ν_1, $B+$)	0.0000	(ν_1, $A+$)
0.0002	(ν_2, $A+$)	0.0003	(ν_2, $B+$)
0.0003	(ν_2, $B+$)	0.0002	(ν_2, $A+$)
0.0000	($2\nu_1$, $A+$)	0.0001	($2\nu_1$, $B+$)
0.0001	($2\nu_1$, $B+$)	0.0000	($2\nu_1$, $A+$)

- N_v = 100 converge all levels to about 0.0001 cm^{-1}.

Conclusions

- Cl^--H_2O rovibrational levels are studied with three methods.
- Method I (old): spherical harmonics basis with polyspherical coordinates
- Method II (new): inter-monomer Wigner basis and intra-monomer vibrational basis
- Method III (new): inter-monomer Wigner basis and vibrational wavefunction basis

- Method III will be very useful for Van der Waals system.

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Wigner basis: the monomer is a rotating-vibrating molecule

- T^A is the standard triatomic rovibrational KEO in a monomer-fixed (MF) bisector frame viewed in a dimer-fixed (DF) frame.

$$T = T^A(\mathbf{j}^{\mathrm{MF},\mathbf{A}}, r_1, r_2, \theta_A) + T_{int}$$

$$T_{int} = -\frac{1}{2\mu_0 r_0^2}\frac{\partial}{\partial r_0} r_0^2 \frac{\partial}{\partial r_0} + B_{r_0}(r_0)\Big[J^2 - i\cot\beta\frac{\partial}{\partial\beta} + j^2 - 2\mathbf{j}\cdot\mathbf{J}\Big]$$

$$T^A = T_v^A + T_{vr}^A$$

$$T_v^A = -\frac{1}{2\mu_{r_1} r_1^2}\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} - \frac{1}{2\mu_{r_2} r_2^2}\frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} - \Big[B_{r_1}(r_1) + B_{r_2}(r_2)\Big]\frac{1}{\sin\theta_A}\frac{\partial}{\partial\theta_A}\sin\theta_A\frac{\partial}{\partial\theta_A}$$

$$T_{vr}^A = \frac{1}{2}\Big[B_{r_1}(r_1) + B_{r_2}(r_2)\Big] \times \Big[\frac{1}{1+\cos\theta_A}(j_x^{\mathrm{MF},A})^2 + \frac{1}{2}(j_y^{\mathrm{MF},A})^2 + \frac{1}{1-\cos\theta_A}(j_z^{\mathrm{MF},A})^2\Big]$$

$$+\Big[B_{r_1}(r_1) - B_{r_2}(r_2)\Big]\Big[\frac{1}{2\sin\theta_A}\{j_x^{\mathrm{MF},A}, j_z^{\mathrm{MF},A}\} - p_{\theta_A}^H j_y^{\mathrm{MF},A}\Big]$$

vibration : $\theta_A, \beta_A, \gamma_A$; rotation : α, β, α_A